ANALYTICAL APPLICATIONS OF MASS SPECTROMETRY

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In the early 1800's, William Prout, an English physician interested in chemical research observed several whole number atomic weights. He hypothesized a whole number of atomic weight system with all atoms being aggregates of hydrogen atoms. Prout's theory was refuted by the failure to obtain weight rectification of any of the elements having chemically determined consistent fractional atomic weights. The concept of mixed atomic masses in an element was considered ridiculous, yet it was not until the positive ray parabola research by J. J. Thompson in 1907 that experimental proof established all atoms of an element at approximately equal mass. By 1910, study of radioactivity and positive ray parabolas indicated that particles of nearly identical chemical activity could have definite mass differences. F. W. Aston is credited with proving the existence of stable isotopes in 1919 with his first mass spectrograph.

During the 1920's, mass spectrographs became popular university research tools. By the 1930's, introductory college physics texts included the simple theory of the mass spectrograph. The short twenty-one years between Aston's invention and the industrial applications of mass spectrometers indicates the value of this tool and illustrates the progressive technical leadership in industry.

The single focusing mass spectrometer is most common in analytical usage. The two principle models commercially available are the 180° magnetic deflection instrument built by the Consolidated Engineering Corporation and the 60° magnetic deflection instrument built by the General Electric Company. In both instruments, the gas or vapor sample is ionized by an electron beam and the positive ions are accelerated by an electric potential, deflected by the magnet and collected one mass at a time. The charge carried by the ions to the collector plate establishes a current in a high resistance between the collector and ground. This signal is amplified and recorded as a measure of the intensity of the ion beam for each mass scanned. The mathematical expression for mass sorting is derived from the two equations:

$$E\,e = \tfrac{1}{2}\,mv^2 \tag{1}$$

$$Hev = \frac{mv^2}{R} \tag{2}$$

where e = charge on the ion, m = mass of the ion, v = velocity of the ion, R = radius of ion path in the magnetic field, E = accelerating potential, and H = magnetic field strength.

Equations (1) and (2) are combined to eliminate the velocity term and result in the expression

$$m/e = H^2\,R^2/2E \tag{3}$$

In the mass spectrometer, the radius of the ion beam path is fixed and the mass range is scanned by varying either H or E. Greater resolution for extremely accurate mass determination is obtained by double focusing instruments that combine electrostatic deflection with magnetic deflection to give optimum focusing of the ion beam. Mass spectrometers are operated at pressures of 10^{-6} mm Hg or less to assure the predominance of primary processes in ionization and to make the mean free path of the ions greater than the path length in the instrument.

In analytical practice, the gas or vapor sample is placed in a large expansion volume at a known pressure and passes into the ionization chamber through a small leak.

Early analytical mass spectrometry was concerned with the identification and abundance of isotopes. A few years later, investigators used mass spectrometry to study molecular dissociation and ionization under electron bombardment. The wartime requirement for large quantities of aviation quality gasoline stimulated the development of complex petroleum processes and a parallel technical advance in analytical control. Thus, the commercial mass spectrometer was developed and became essential to the petroleum industry for quantitative analysis and process control (Washburn, Wiley, and Rock, 1943).

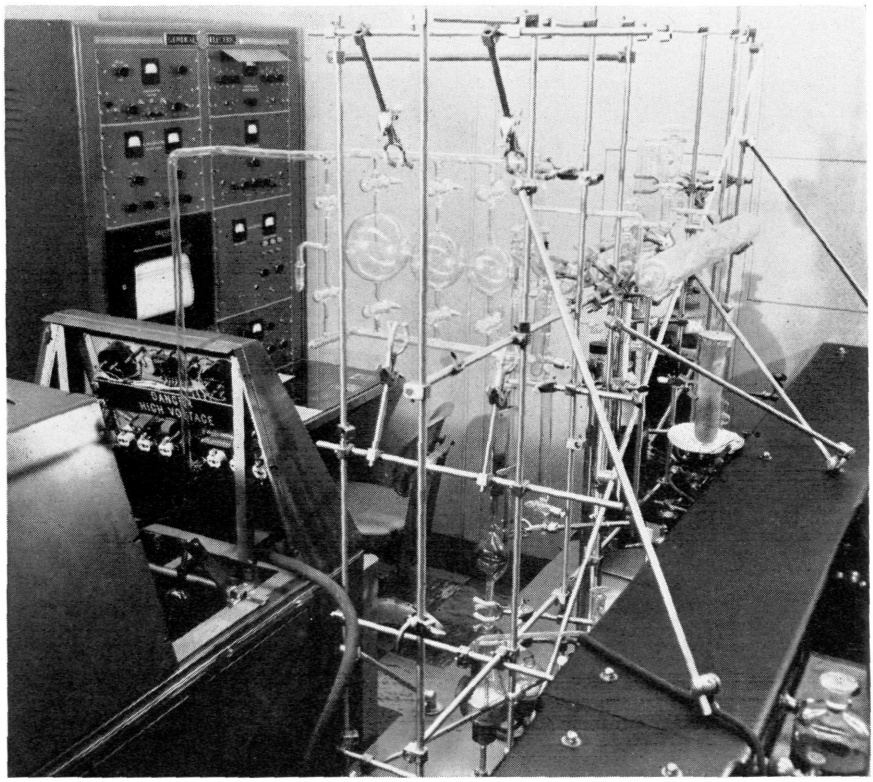

FIGURE 1. Photograph of the B. F. Goodrich Company Research Center General Electric Instrument. The spectrometer tube rack is in the lower left, the control cabinet is in the background, and the locally built sample system is shown at the right.

By using ionizing electrons with energies well above the dissociation energies for chemical bonds, the mass spectrometer records cracking patterns containing nearly all possible segments of the molecule. Nearly all molecules including isomers have cracking patterns that may be used qualitatively for identification and in most cases quantitatively for analysis in mixtures. Table 1 shows the cracking pattern of a commercial grade acetone. The mass 31 peak is rearrangement ion of CH_3O^+ form and is commonly found in oxygenated compounds. Cracking patterns differ somewhat from instrument to instrument, and even change with time for the same instrument due to uncontrolled factors. This necessitates calibration runs with pure compounds for every instrument for quantitative

analysis. For qualitative application, over 500 mass spectral data sheets have been published by the American Petroleum Institute Research Project No. 44.

The cracking pattern offers qualitative information to an experienced operator. Indications of compound purity are easily obtained by comparison of patterns. Often impurities may be recognized by the presence of peaks not consistent with the sample examined. Familiarity with masses and natural abundance of isotopes

TABLE 1

Cracking pattern of acetone at 70 volts ionization energy

m/e	Intensity	Remarks
12	0.43	C^+
13	1.14	CH^+
14	4.46	CH_2
15	25.73	CH^+_3
16	0.48	O^+ and rearrangement to CH^+_4
17	0.31	OH^+
18	1.22	H_2O^+
19	0.25	Doubly charged mass 38 ion
19.5	0.14	Doubly charged mass 39 ion
20	0.12	Doubly charged mass 40 ion
24	0.18	C^+_2
25	1.02	C_2H^+
26	4.41	$C_2H_2^+$
27	6.54	$C_2H^+_3$
28	8.99	CO^+
29	2.82	Isotope peak and rearrangement to COH^+
30	0.09	Isotope peak
31	0.47	Rearrangement to CH_3O^+
36	0.52	C_3^+
37	1.74	C_3H^+
38	2.14	$C_3H_2^+$
39	4.08	$C_3H_3^+$
40	0.82	$C_3H_4^+$ and C_2O^+
41	1.82	$C_3H_5^+$ and C_2HO^+
42	6.70	$C_3H_6^+$ and $C_2H_2O^+$
43	*100*	$C_2H_3O^+$ (Base Peak)
44	2.58	Isotope peak and rearrangement $C_2H_4O^+$
45	0.26	Isotope peak
50	0.19	Impurity
51	0.47	Impurity
52	0.27	Impurity
53	0.42	Impurity
54	0.05	$C_3H_2O^+$
55	0.29	$C_3H_3O^+$
56	0.04	$C_3H_4O^+$
57	0.79	$C_3H_5O^+$
58	26.48	$C_3H_6O^+$ (Parent peak)
59	0.90	Isotope peak
60	0.05	Isotope peak

often permits identification of certain elements in a compound and may indicate the number of such atoms present. In some cases, structural characteristics are determinable together with indications of molecule stability.

The majority of organic analyses done with mass spectrometers are quantitative. These require a knowledge of components present and a cracking pattern of each component. This is the type analysis important to the petroleum industry. Special computers have been built to permit the analysis of mass spectral data of petroleum fractions for twelve or more components in a matter of minutes. Speed

and accuracy make these analyses ideal for petroleum process control. Table 2 shows a sample cracking pattern and how it is made up of contributions to peaks from its components. Knowing the sensitivities for each component and the amount of sample introduced, the quantitative analysis of the mixture is straightforward.

During the past four years, Madorsky and coworkers (1949) at the National Bureau of Standards have reported pyrolytic techniques for the study of polymeric materials in the mass spectrometer. Their method involves the controlled thermal

TABLE 2

A sample cracking pattern showing contributions of components.

m/e	Original Sample	Propane Contribution	Original Minus Propane	Ethane Contribution	Original Minus Propane and Ethane	Methane Contribution	Remainder
12	2.15	0.28	1.87	0.34	1.53	1.51	+0.02
13	6.52	0.69	5.83	0.82	5.01	5.01	....
14	15.0	2.49	12.5	2.45	10.0	10.01	−0.01
15	66.2	8.26	57.9	3.60	54.3	54.3	
16	64.2	0.11	64.1	0.10	64.0	64.0	
26	30.4	11.5	18.9	18.9			
27	78.5	51.5	27.0	27.0			
28	164.9	83.4	81.5	81.5			
29	157.3	139.8	17.5	17.5			
30	24.4	3.07	21.3	21.3			
31	0.44	....	0.44	0.44			
38	6.54	6.54					
39	24.5	24.5					
40	3.68	3.68					
41	18.1	18.1					
42	8.22	8.22					
43	32.4	32.4					
44	41.0	40.9	0.01	....	0.01	....	0.01

degradation of polymers in vacua and the immediate immobilization of the reactive fractions by cold trapping. The five fractions collected in the process are:

1. Non-volatile residue.
2. Wax-like residue volatile at pyrolysis temperature.
3. Low volatility liquid.
4. High volatility liquid.
5. Fraction gaseous at liquid nitrogen temperature.

Most of the reported study has involved the liquid fractions. The pyrolytic technique for the study of polymers offers definite polymer identification, indicates purity, and offers promise in the investigation of correlation between structural formulae and physical and chemical properties.

Preliminary success has been reported in the study of reaction intermediates by means of a mass spectrometer (Eltonten, 1947). By coupling the instrument directly to a reaction vessel, the presence of short-lived radicals has been demonstrated. Some of the lower mass radicals have been identified and proven to be a product of the reaction. Operation of the reaction vessel over a wide temperature range has shown correlation between ion intensities and the thermal cracking of hydrocarbons. This technique is extremely sensitive—capable of detection of about five parts per million of free radical concentration. There is promise of successful investigation of high speed reactions such as flame study by probing the reaction area with a mass spectrometer.

In a discussion of recent developments in mass spectrometry at the Buffalo Instrument Conference (1950), M. G. Inghram stated that sensitivities up to 10^4 times that of ordinary wet chemical methods were possible in inorganic mass spectral analysis. Isotope dilution techniques have been established for quantitative analysis of low volatility inorganic materials. Similar methods have been used to determine reactions of impurities in slow neutron induced reactions. Daughter isotopes of different mass are added before a reaction and isotope abundance comparison with undiluted reaction material yields quantitative results (Hayden, Reynolds, and Inghram, 1949).

Either short half-lives or limited availability of radioactive isotopes of such common elements as hydrogen, nitrogen, potassium, and oxygen makes mass spectral stable isotope tracer study important to the chemist. As yet, low enrichments and limited supplies of stable isotopes have restricted mass spectral tracer studies. All isotopes of an element are not strictly identical in chemical behavior since bond strength is influenced by atomic mass. This difference is most notable in the case of hydrogen and deuterium and decreases with increasing mass. The dissociation of bonds between light isotopes are more probable than the dissociation between heavier isotopes. For example, the dissociation of the C^{12}-O^{16} bond is about 3.5% more frequent than for the C^{12}–O^{16} bond after allowance is made for the relative abundances of C^{12} and C^{13} isotopes. These variations are noted in thermal dissociation as well as in electron dissociation in the mass spectrometer.

Any routine stable isotope enriched tracer study will require compensation for isotope effects in cracking patterns. Since these effects will increase in complication with the complexity of the molecules and the number of tracer atoms, isotope exchange with less complicated compounds will be applied.

Stable isotope tracer experiments are particularly useful in biological research. Compounds labeled with N^{15} have been used to investigate incorporation of the compounds in proteins. Rates of protein synthesis in different organs are measured. The metabolism of carbohydrates has been investigated by using deuterium and C^{13} stable isotopes as well as radioactive P^{32} and C^{14}. Tracer compounds become quite diluted in most experiments. This means that success is generally limited to elements having low natural abundance of the tracer isotope. Stable isotope tracer work becomes difficult, if not impossible, in the case of elements such as iron and chlorine. Fortunately, in most of these cases there are now available radioactive isotopes of satisfactory half-life. An excellent account of the use of stable and radioactive isotopes in biological research is in *Isotopes in Biology and Medicine* by nineteen leaders in fields of physics, chemistry, physiology, and medicine; The University of Wisconsin Press (1948).

The mass spectrometer has proven itself in the petroleum industry as an essential analytical and process control instrument. Mass spectrometers are currently entering such diverse industries as chemical, rubber, glass, air products, meat packing and food processing, metal, and aircraft products. The manufacturers of mass spectrometers are conducting extensive instrument research and development programs. The Bennett type radio frequency mass sorting tube and the ion resonant tube are promising new developments applicable to the lower mass region for leak detection and process control.

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